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**CATALYTIC DECHLORINATION OF HD
WITH A QUATERNARY AMMONIUM PHASE-TRANSFER CATALYST**

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13. ABSTRACT (Maximum 200 words) The objective of this research was to characterize the effects of the quaternary ammonium compound, dodecyldimethyl(3-sulfopropyl)ammonium hydroxide (DDSAH), with respect to its effects on the dechlorination of HD. It was previously observed that this compound, as well as several other quaternary ammonium and phosphonium compounds, increased the rate of HD dechlorination. The objective of this study was to quantitate the effects of DDSAH under a variety of conditions of concentration, temperature, and pH and to determine if the effect was in fact catalytic. In general, the effects of DDSAH were relatively insensitive to pH over the range of 6.0 to 8.5, and relatively more sensitive to temperature, in that the effects on the dechlorination rate increased fairly sharply above 35 °C. With respect to DDSAH concentration, effects varied less than three-fold over a 1000-fold concentration range between 0.01 and 10 mg/mL. The effects of HD concentration varied about three-fold between 0.5 and 5 mg/mL. Evidence for catalysis was based on the observance of a 75% dechlorination rate increase resulting from the addition of 1.5 mM DDSAH to a 16 mM HD reaction.				
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PREFACE

The work described in this report was authorized under Project No. 611384/ACB1, Non-Medical CB Defense. This work was started in April 1998 and completed in December 1998.

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CATALYTIC DECHLORINATION OF HD WITH A QUATERNARY AMMONIUM PHASE-TRANSFER CATALYST

1. INTRODUCTION

For purposes of HD decontamination, hydrolysis is an advantageous reaction, since the primary product, thiodiglycol, is approximately 5,000 times less toxic than HD, on an LD₅₀ basis¹⁻². However, HD is essentially insoluble in water, which causes the hydrolysis reaction rate to be exceedingly low in the absence of agitation or heat³.

Dr. Charles Starks coined the term "Phase Transfer Catalysis" in 1987 to describe the rate enhancement of some reactions in the presence of compounds like quaternary ammonium salts⁴. In 1996, there were several commercial processes that used approximately on million lbs per year each of phase-transfer catalysts (PTC)⁵. However, the catalytic activity of quaternary ammonium salts was first patented in 1912⁶ and apparently first used commercially in 1946 to produce butyl benzyl phthalate from sodium monobutyl phthalate and benzyl chloride⁷.

Many theories have been proposed to explain PTC action, but they briefly can be described by two mechanisms, i.e., the *extraction* and *interfacial* mechanisms. These terms loosely refer to whether the rate-determining step of the reaction occurs in the organic phase with transferred reagent, or whether it occurs at the interface. In practice, both mechanisms probably operate with varying rates for most reactions⁸. Since the HD hydrolysis rate is proportional to stirring speed throughout at least part of the reaction regime, its phase-transfer catalysis would presumably be explained at least in part by the interfacial mechanism.

2. MATERIALS AND METHODS

HD was Chemical Agent Standard Analytical Reference Material and was greater than 97% pure. HD was diluted to 10 vol % in dry methanol prior to use. HD chloride release was measured with a chloride-specific electrode calibrated against known standards. Reactions were conducted in 2.5 ml volumes in temperature-controlled vessels with controlled agitation rates provided by a magnetic stir bar.

Dodecyldimethyl(3-sulfopropyl)ammonium hydroxide was purchased from Aldrich and was 99% pure.

3. RESULTS

Potential catalysts were typically screened by monitoring the complete chloride release from 6.25 mg HD in 2.5 ml of 50 mM bis-tris-propane buffer, pH 7.2 at 25-35° C with moderate and controlled electronic stir bar agitation. The reaction was essentially complete in 25-30 minutes (primarily depending on temperature) and the reaction profile

was plotted on a percentage basis to correct for electrode interferences caused by some of the catalysts. Rates in buffer alone were compared to those in the presence of 0.5-2 mg/ml of the catalyst. Most materials produced little or no difference in reaction profile. A notable exception was dodecyldimethyl(3-sulfopropyl)ammonium hydroxide (DDSAH) (Figure 1). DDSAH is a zwitterionic species and is a powder at room temperature.

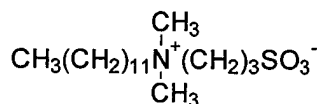


Figure 1. Dodecyldimethyl(3-sulfopropyl)ammonium hydroxide (FW 335.5).

Figure 2 shows the dechlorination profile 2.5 mg/ml HD, alone and in the presence of 0.5 mg/ml DDSAH, at 25° C and pH 7.2. The initial rate is clearly greater in the presence of a relatively small amount of the quaternary ammonium compound.

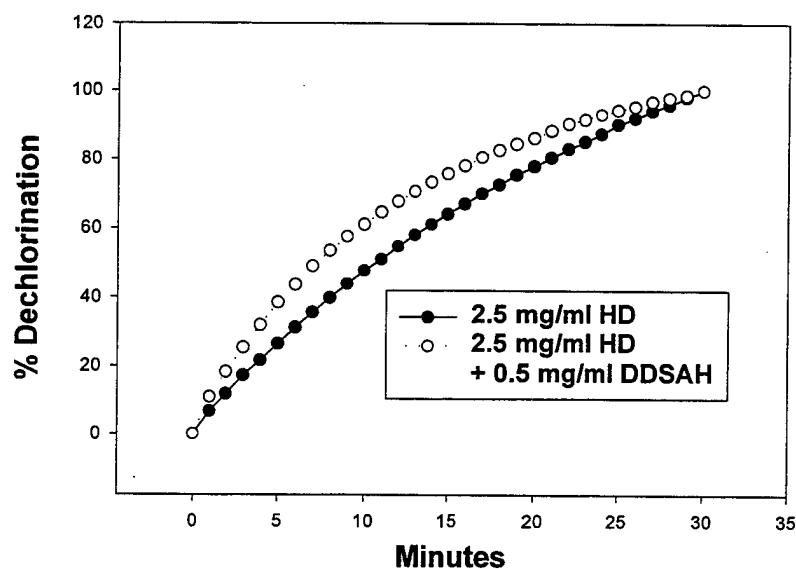


Figure 2. Reaction profile of DDSAH and control.

Since it is evident from Figure 2 that the presence of DDSAH was increasing the reaction rate, effects of DDSAH concentration, HD concentration, temperature and pH were investigated. Figure 3 shows the effects of DDSAH concentration over a 1,000-fold range (0.01 to 10 mg/ml). For all values, the background dechlorination rate in the

absence of catalyst was subtracted from that observed in the presence of catalyst. Optimal rates were generally achieved in the range of 0.5 to 5 mg/ml.

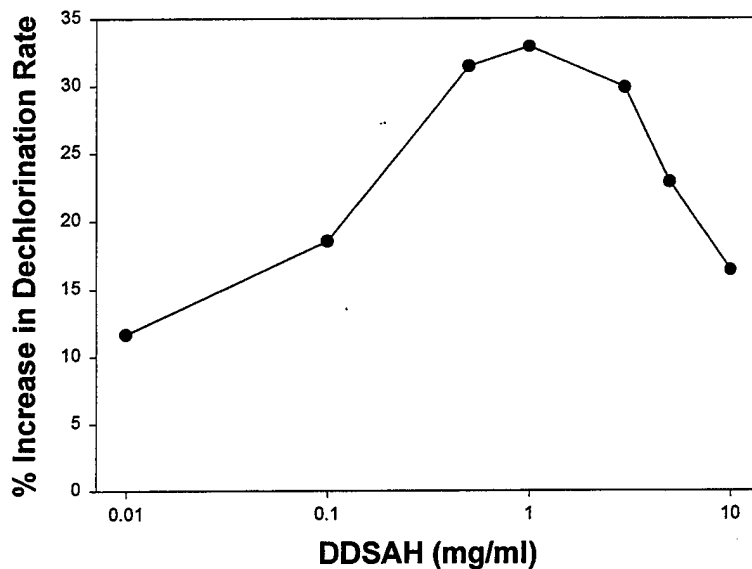


Figure 3. Effects of DDSAH concentration on the HD dechlorination rate.

The effects of HD concentration were also investigated over a 10-fold range (0.5 to 5 mg/ml). The optimal concentration was near 2 mg/ml (Figure 4).

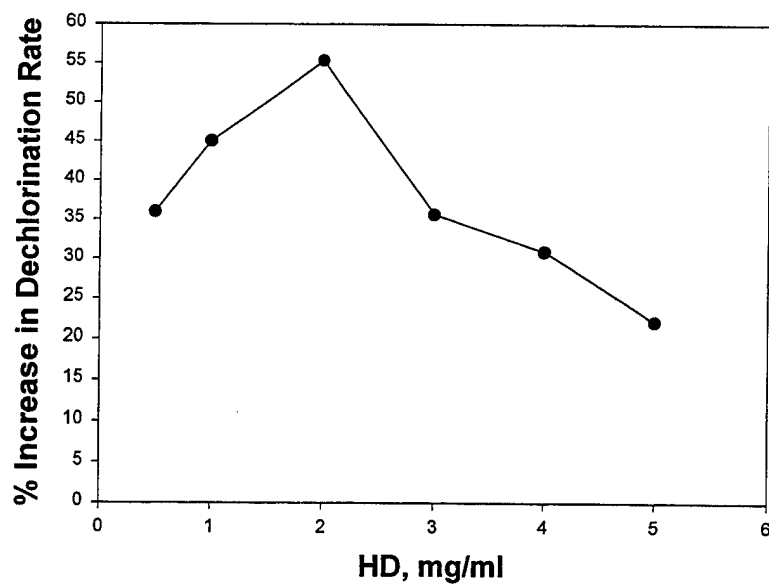


Figure 4. Effects of HD concentration on the rate of DDSAH-catalyzed HD dechlorination.

The effects of pH were investigated between 6 and 8.5 (Figure 5). Below pH 6.0, bis-tris propane offered little buffering capacity; above pH 9.0 the background hydrolysis rate was too high to permit reproducible rate determinations. In general, little effect of pH was observed over the range tested.

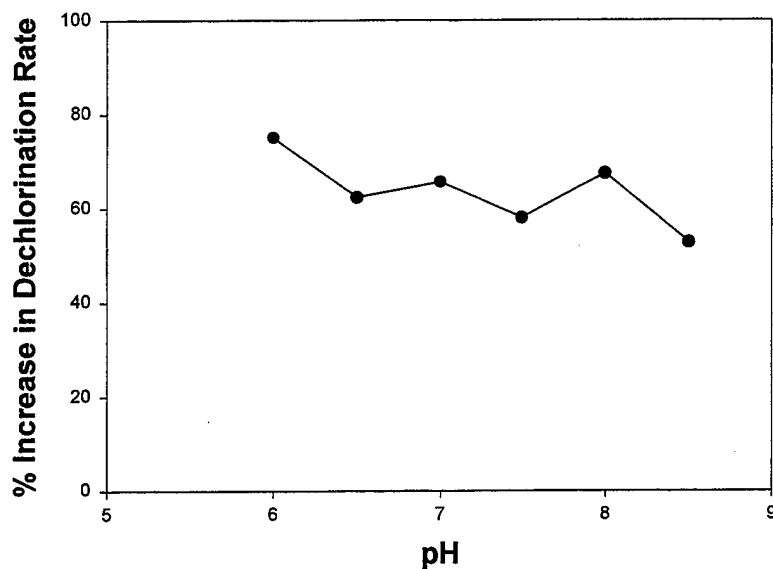


Figure 5. Effect of pH on the rate of DDSAH-catalyzed HD dechlorination.

The effects of temperature were investigated over a range of 20° C to 50° C (Figure 6). HD freezes at 15° C and hydrolyzes too rapidly above 50° C, so this was the approximate range within which reproducible rates could be measured. Between 20° and 35°, little change was observed. At higher temperatures of 40-50°, the catalyst effect was almost twice that observed at the lower temperatures.

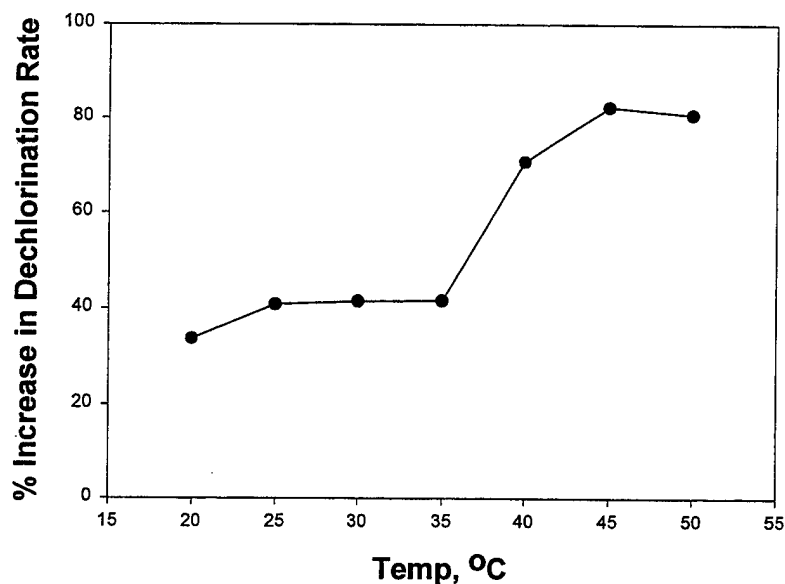


Figure 6. Effect of temperature on the rate of DDSAH-catalyzed HD dechlorination.

By definition, catalysis involves the enhancement of reaction rate by the addition of a relatively small amount of a non-reactant material. One powerful line of evidence for catalysis is based on stoichiometry; if the observed effects cannot be accounted for on a stoichiometric basis, then catalysis is a logical explanation. In order to study this effect, a reaction was set up using 2.5 mg/ml HD and 0.5 mg/ml DDSAH (16 mM HD and 1.5 mM DDSAH). With these concentrations of materials, at pH 7.2 and 25° C, a 75% rate enhancement was observed (Table 1). The entire reaction profile is shown in Figure 2 above. The observation of a 75% dechlorination rate increase from the addition 1.5 mM DDSAH to a 16 mM HD reaction is consistent with a catalytic effect of the DDSAH on this reaction.

Table 1. Evidence for DDSAH catalysis.

Reaction	[HD]	Effective HD Molarity	[DDSAH]	DDSAH Molarity	Rate (ppm Cl- min ⁻¹)	% Rate Increase
HD Alone	2.5 mg/ml	16 mM	none	none	35.4	N/A
HD + DDSAH	2.5 mg/ml	16 mM	0.50 mg/ml	1.5 mM	61.9	75%

One explanation of the DDSAH-catalyzed dechlorination of HD could be via a mechanism similar to that postulated for the cyanide displacement reaction⁹. It should be noted though, that other PTC-catalyzed reactions have been shown to simultaneously proceed via more than one mechanism.

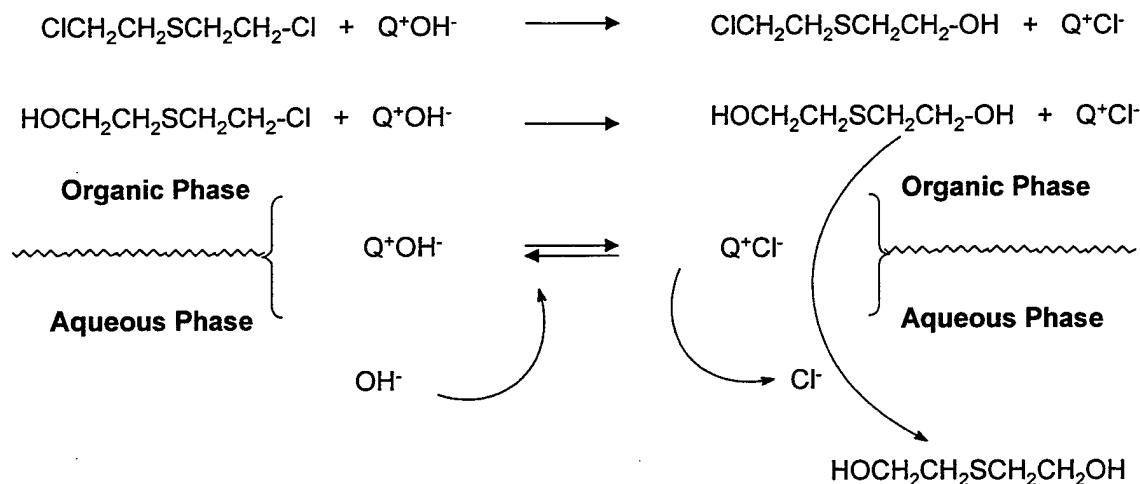


Figure 7. Concept diagram of DDSAH catalysis of HD dechlorination. Adapted from Starks⁹. Hydroxide ion from the aqueous phase is transferred via the quaternary ammonium compound (Q⁺) through the aqueous/organic interface. In the organic phase, chloride groups are successively removed from HD. The resulting Cl⁻ is transferred through the interface as Q⁺Cl⁻. The final product, thiodiglycol (HOCH₂CH₂SCH₂CH₂OH), dissolves in the aqueous phase, eventually eliminating the organic phase altogether.

4. CONCLUSIONS

DDSAH was observed to accelerate HD dechlorination over a relatively wide range of reactant and catalyst concentrations, temperature and pH. Evidence for catalysis was provided by the demonstration of a 75% dechlorination rate increase from the addition of 0.5 mg/ml (1.5 mM) DDSAH to a reaction of 2.5 mg/ml (16 mM) HD. While HD is known to hydrolyze under these conditions, yielding primarily thiodiglycol as the product, it is not yet certain that this is the case for the DDSAH-catalyzed reaction, although that would be consistent with these data. Since only the dechlorination rate was measured for these experiments, it is possible though, that DDSAH produces an elimination reaction, in addition to or instead of the hydrolysis reaction. Definitive reaction evidence awaits product analysis. However, it is clear from these data that the rate of HD dechlorination is accelerated by the addition of a relatively small amount of DDSAH under a variety of conditions.

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